OPTICAL PROPERTIES OF 2-(2',4'-DINITROBENZYL)-PYRIDINE IN THE ADSORBED STATE

By G. Kortum,[1] M. Kortum-Seiler,[1] and S. D. Bailey

Contribution from the Pioneering Research Division,
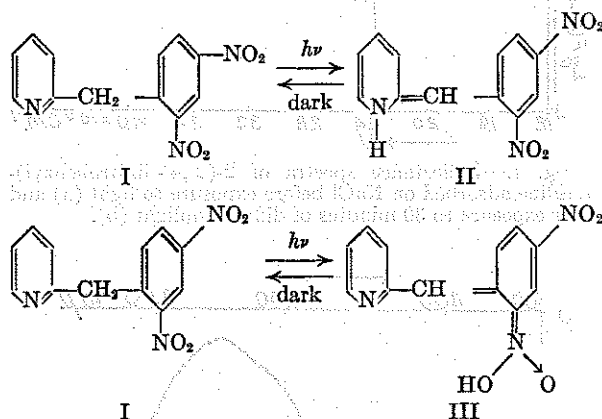*Quartermaster Research and Engineering Center, Natick, Mass.*

Diffuse reflectance spectroscopy has been used in an investigation of the reversible photochemical conversion of 2-(2',4'-dinitrobenzyl)-pyridine in the adsorbed state. The tautomeric shift associated with this conversion was studied in the phase boundary of those adsorbents which serve as electron acceptors. Two first order reactions were found which probably are due to the fading of a positive ion and of the neutral molecule, respectively. Activation energies have been estimated from the kinetic data.

The Kubelka–Munk theory,[2] describing the process of "diffuse reflectance" of finely powdered absorbing material, has not been extensively used because the invariably superimposed "regular reflectance" levels and broadens the derived spectra. To get the true absorption spectrum from reflectance measurements one therefore has to eliminate the regular part of the reflection. This can be done easily by triturating the sample together with a large excess of a non-absorbing standard of the same particle size.[3,4] Since in this process all organic and many inorganic compounds are adsorbed on the surface of the standard, this method is especially suitable for the investigation of the optical behavior of adsorbed molecules.

Recent work, for instance on the reversible adsorption of different dyes on surfaces of appropriate adsorbents,[5,6] has shown that frequently a chemisorption is taking place which is accompanied by a pronounced change of color. This can be attributed to an electron-donor-acceptor-process between adsorbed material and the adsorbent. Equally, irreversible photochemical reactions of adsorbed molecules have been investigated by this method.[7] The method, therefore, appeared promising for the investigation of the reversible photochemical reaction of 2-(2',4'-dinitrobenzyl)-pyridine, which turns blue by illumination and fades again in the dark to its original colorless form. This reaction takes place in the crystalline form as well as in solution,[8] but the rate of fading in solution is very rapid and can only be observed at low temperatures[9] or by a special flash technique at room temperature.[10]

The reaction has been interpreted[8] as a tautomeric shift which involves either the pyridine or the neighboring nitro group.

(1) Visiting scientists from the Institute for Physical Chemistry, University of Tübingen, Tübingen, Germany.

(2) P. Kubelka and F. Munk, *Z. Techn. Phys.*, **12**, 513 (1931); P. Kubelka, *J. Opt. Soc. Am.*, **38**, 448, 1067 (1948).

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(7) G. Kortum and W. Braun, *Ann. Chem.*, **632**, 104 (1960).

(8) R. Hardwick, H. S. Mosher, and P. Passailaigue, *Trans. Faraday Soc.*, **56**, 44 (1960); H. S. Mosher, C. Sauers, and R. Hardwick, *J. Chem. Phys.*, **32**, 1888 (1960).

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We have studied this reaction in the phase boundary of several adsorbents by measuring the reflectance spectra of mixtures, where the molar fraction of the nitro compound was 10^{-3} to 10^{-4}, against the pure adsorbent as standard. Adsorption was accomplished by grinding for several hours in a ball mill in the dark in a CO_2 atmosphere. The sample then was exposed to diffuse daylight for 30 minutes and measured again. The spectra on NaCl as adsorbent are shown in Fig. 1.

The logarithm of the Kubelka–Munk function

$$F(R_\infty) \equiv \frac{(1 - R_\infty)^2}{2R} = \frac{\epsilon c}{s}$$

is plotted against the wave number. $R_\infty \equiv I(\text{sample})/I(\text{standard})$ is the measured relative diffuse reflectivity, ϵ the molar extinction coefficient, c the molarity, and s the scattering coefficient, which is essentially independent of the wave length. The spectra are therefore identical with the true absorption spectra, except for a parallel shift in the values of log ϵ. Quite analogous spectra were obtained on silica and lithium fluoride as adsorbents. Prolonged irradiation changes the compound irreversibly both in the case of the pure substance and in the solutions.[8]

The adsorbed nitro compound when illuminated turns blue, like the pure crystalline compound (λ max $\cong$ 600 mμ), with the color fading slowly over a period of about 10 hours in the dark. The spectrum can be measured easily therefore at room temperature.

Since earlier studies had shown that the interaction between adsorbed molecules and the adsorbent can in some cases be prevented by adsorbed
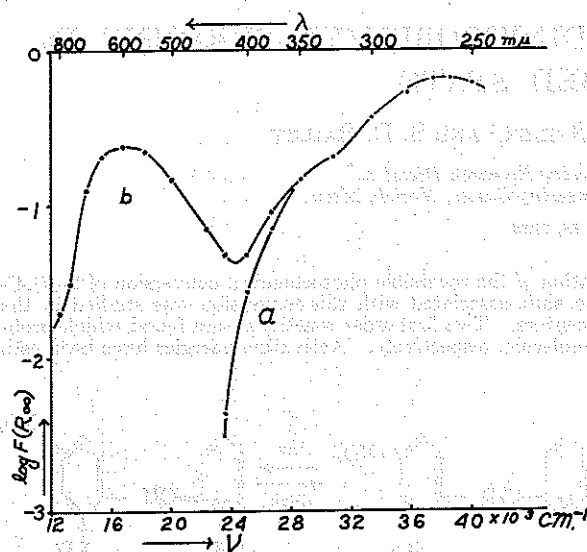
Fig. 1.—Reflectance spectra of 2-(2',4'-dinitrobenzyl)-pyridine adsorbed on NaCl before exposure to light (a) and after exposure to 30 minutes of diffuse sunlight (b).
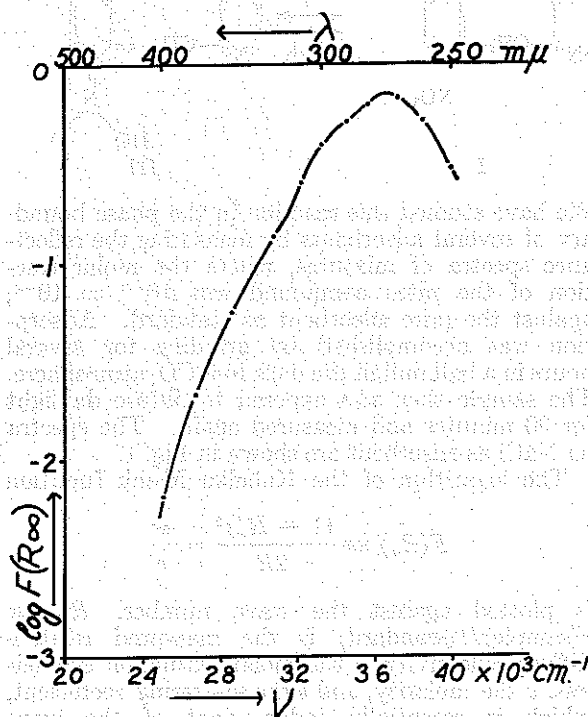

Fig. 2.—Reflectance spectrum of 2-(2',4'-dinitrobenzyl)-pyridine adsorbed on magnesium oxide.

water,[5,6] we at first carried out all experiments in the absence of moisture by heating the adsorbents to 500° for several hours and sealing the sample cells with quartz plates in a glove-box in a dry carbon dioxide atmosphere. It was found, however, that the exposure of the adsorbed and converted compound to moist air did not change the intensity of absorption, so that later experiments were made with adsorbents which were air-dried only. The strong partial dipole moments of the nitro compound appear to be capable of displacing the water molecules from the surface of the adsorbent.

Quite unexpectedly the conversion to the blue form by illumination failed when the compound was adsorbed on MgO. Instead, an irreversible reaction in the dark took place, indicated by two maxima in the visible region at about 670 and 480 $m\mu$, respectively, which did not change upon irradiation in the ultraviolet. This is shown in Fig. 2. This reaction, in contrast to the tautomeric shift, seems to be accelerated by water and can best be investigated on adsorbents which are only air-dried.

An indication of the reaction mechanism was given by earlier experiments[5] on the reflectance spectra of s-trinitrobenzene adsorbed on MgO. Whereas s-trinitrobenzene adsorbed on SiO_2 or NaCl remains colorless, the adsorption on MgO produces a bright red compound, the spectrum of which is analogous to that of an alkaline solution of the same compound in water. This reaction has been explained according to polarographic investigations[11] as an addition of OH^- ions on the benzene nucleus:
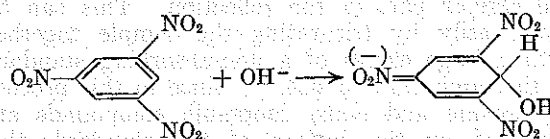
We therefore triturated 2,4-dinitrotoluene with an excess of MgO and SiO_2, respectively, and found that it reacts with MgO in the same way whereas on silica it remains unchanged.

We may therefore conclude that an analogous reaction takes place between the dinitro compound and MgO at the phase boundary, the MgO acting as an electron donor
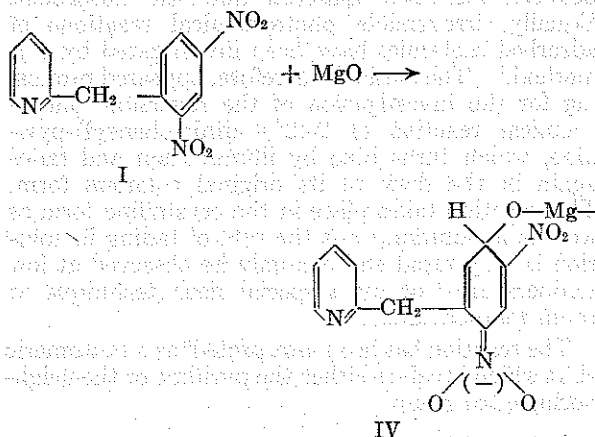
The quinoid structure of this compound explains the absorption in the visible and prevents the conversion I → III, but would not prevent the tautomeric reaction I → II. From the fact that the dinitro compound does not turn blue on MgO by illumination we conclude that the mechanism of this conversion consists more likely in an intramolecular shift I ⇆ III than in a shift I ⇌ II. This can be confirmed further by the optical behavior of the 2-(4'-nitrobenzyl)-pyridine, in which

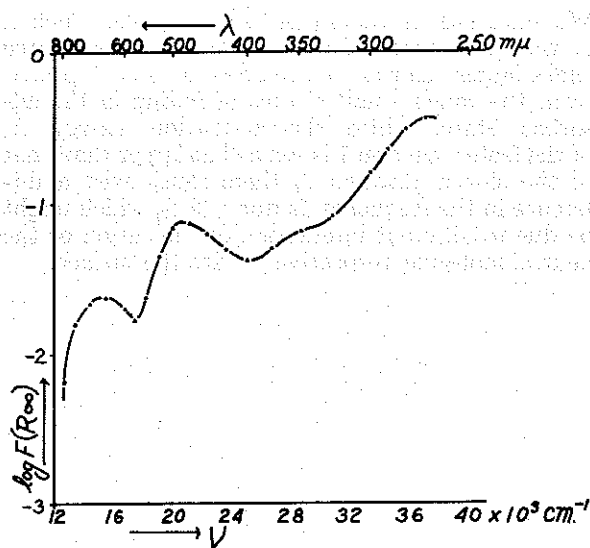(11) L. Holleck and G. Perret, Z. Elektrochem., **59**, 114 (1955); **60**, 463 (1956).

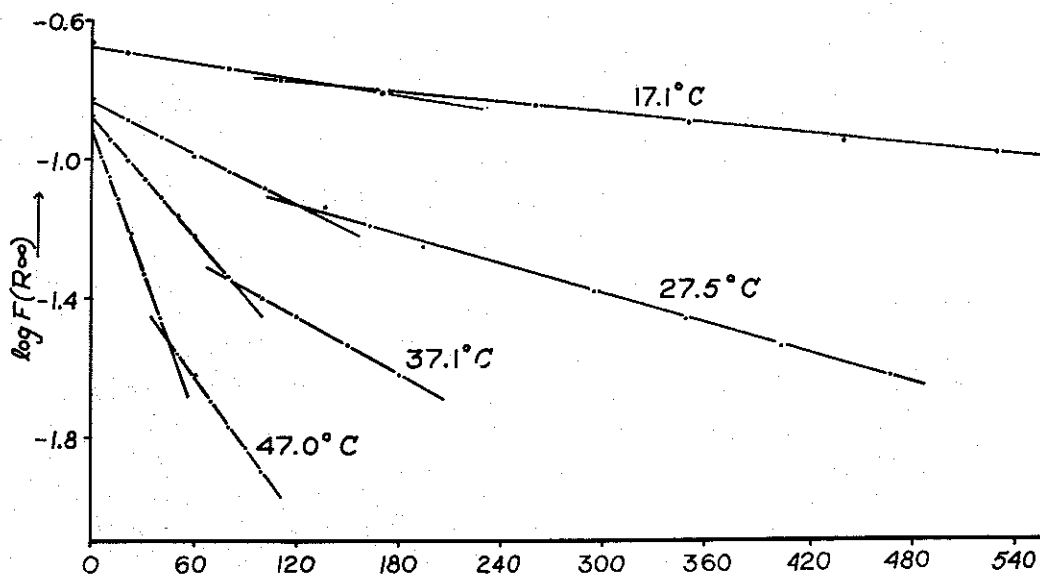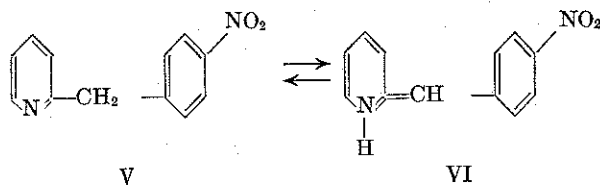Fig. 3.—Reflectance spectrum of 2-(4′-nitrobenzyl)-pyridine adsorbed on silica.

does not occur.   Neither does the irreversible reaction I → IV take place on $MgCO_3$ and Al_2O_3. In the case of CaO it can be detected slightly.   On very pure "neutral" Al_2O_3 the tautomeric shift I → III can be observed, but to a lesser degree than on SiO_2, NaCl, or LiF, all other conditions being held constant.

In order to compare our results with those in solutions, we have made rate measurements of the fading reaction III → I as a function of temperature using silica as the adsorbent.   For this purpose the samples were sealed in fused quartz cells which could be kept in a water thermostat and which were measured against the pure adsorbent as reference at 600 mμ as a function of time t.   The logarithm of the Kubelka–Munk function log $F(R_\infty)$ plotted against t at four different temperatures is shown in Fig. 4.   Obviously there are two first order reactions with different rates which are analogous to reactions in solution at different pH's.[10]   This may be attributed to the fading of the cation

Fig. 4.—Fading reaction of 2-(2′,4′-dinitrobenzyl)-pyridine as a function of temperature: plot of log $F(R_\infty)$ vs. time in minutes at temperatures of 17.1, 27.5, 37.1 and 47.0°.

the analogous tautomeric shift to I ⇌ II would be expected to take place
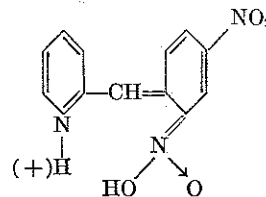

V   VI

By this reaction a resonance system extending over the whole molecule should result, giving a shift of the absorption to longer wave lengths.   The reflectance spectrum of the mononitro compound adsorbed on air-dry silica (Fig. 3) was measured and no shift in the absorption was found.   This means that the reaction V → VI is very unlikely.

$MgCO_3$, CaO, and "alkaline" Al_2O_3 as adsorbents behave in the same manner as MgO in that the conversion to the blue form upon irradiation

and of the neutral molecule (I), respectively, the proton being substituted by acid groups —Si—OH.

From the slopes of the straight lines the rate constants k of the two reactions can be calculated and are given in Table I.

The values of log k plotted against $1/T$ give approximately straight lines, the slopes of which give the activation energies E for the two fading reactions

$$-\frac{2.30R\Delta \log k}{\Delta(1/T)} = E$$

Table I

°C.	1/T	k_1 min.$^{-1}$	$\log k_1$	k_2 min.$^{-1}$	$\log k_2$
47.0	0.00312	0.0307	−1.513	0.0160	−1.796
37.1	0.00322	0.0128	−1.893	0.0061	−2.213
27.5	0.00333	0.0057	−2.240	0.0032	−2.492
17.1	0.00345	0.0017	−2.771	0.0011	−2.947

We find $E_1 \cong 17$ and $E_2 \cong 15$ kcal./mole, which is of the same order of magnitude and about three times larger than in solution,[9] as is to be expected from the much smaller rates of fading in the adsorbed state. Since the activation energy E_1 of the faster reaction 1 is somewhat larger than that of the slower reaction 2, there must exist a difference in the frequency factor $f_1 > f_2$, which might be due to different interaction of the cation or the neutral molecule, respectively, with the surface.